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Supplementary Information

Room Temperature Heliconical Twist-Bend Nematic Liquid Crystal

Yuan Wang,[†] Gautam Singh,[‡] Dena M. Agra-Kooijman,[‡] Min Gao,[†] Hari Krishna Bisoyi,[†] Chenming Xue,[†] Michael R. Fisch,[§] Satyendra Kumar,[‡] and Quan Li[†,*]

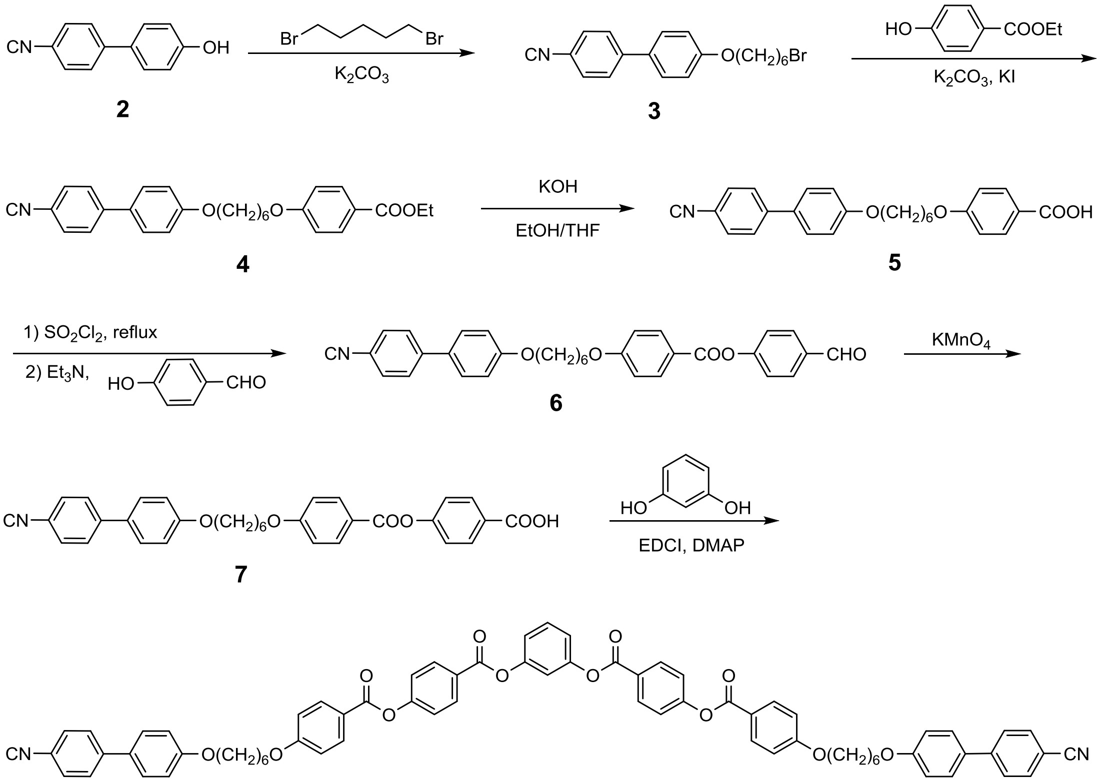
[†]Liquid Crystal Institute, [‡]Department of Physics, and [§]College of Applied Engineering Sustainability and Technology, Kent State University, Kent, Ohio 44242, USA

1. Materials and Methods

All starting material, solvents and reagents were purchased from Sigma-Aldrich company and used without further purification. Colunm chromatography was carried out on silica gel (230-400 mesh). Analytical thin layer chromatography (TLC) was performed on commercially coated 60 mesh F254 glass plate. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker 400 spectrometer. Chemical shifts are reported in units (ppm) with the residual sovlent peak as internal standard. Elemental analysis was performed by Roberston Microscopy Inc. Calorimetric measurements were performed on Universal V3.9A TA instruments (scanning rate 5°C/minute). Transition temperatures were taken at the maximum of transition peaks. The optical textures were recorded by using high-resolution optical polarizing microscope (OLYMPUS BX51), equipped with CCD device (SPOT, Diagnostic Instruments, inc. USA). The textural measurements were done on unaligned, homogeneously and homeotropically anchored sample cells placed on Mettler Hotstage (FP82HT) attached with temperature controller (FP90) with thermal stability of of ±0.1°C. The polyimides SE7492 and S60702 were used for homogenous and homeotropic anchoring of sample. X-ray diffraction measurements were carried out by using the Rigaku Screen Machine with microfocus sealed X-ray tube with Copper anode (λ=1.541870Å). Sample was filled into a quartz capillary of 1.5 mm diameter and then capillary was flame sealed. The capillary sample was placed between a pair of rare earth permanent magnets inside the hot stage (INSTEC HS402) with temperature stability of ±0.1°C. The diffraction patterns were recorded by using high resolution

Mercury 3 CCD detector positioned 64.24 mm away from the capillary sample. The 2D diffraction patterns were analyzed by using FIT2D software after subtracting the background measured with an empty capillary in the sample position or isotropic scattering. The data was calibrated against silver behenate or silicon standards traceable to the National Institute of Standards and Technology. FFTEM experiment: To prepare the replica for FFTEM, the material was heated to achieve isotropic phase and cooled slowly to 50°C at which the sample was stablized to obtain the Ntb phase. The sample was then plunge frozen in liquid nitrogen and fractured at $T = -150^{\circ}\mathrm{C}$ in a BalTec BAF060 freeze fracture apparatus. The fractured surface was replicated by the deposition of Pt/C (4 nm in thickness) at 45°, followed by the deposition of a 20 nm C film. The replica was collected on carbon coated TEM grids and observed using a FEI Tecnai F20 TEM.

2. Synthesis of Hybrid Bent-core Liquid Crystal Trimer 1



bent-core liquid crystal trimer **1**

2.1. Ethyl 4-((6-((4'-isocyano-[1,1'-biphenyl]-4-yl)oxy)hexyl)oxy)benzoate (4)

To a solution of 1,6-dibromohexane (7.71 g, 30 mmol) in butanone (100 mL) was added K_2CO_3 (2.76 g, 20 mmol) and 4’-hydroxy-4-biphenylcarbonitrile (1.00 g, 5 mmol). Then the mixture was refluxed for 1 h. After adding another portion of 4’-hydroxy-4-biphenylcarbonitrile (1.00 g, 5 mmol), the mixture was refluxed for 48 h. The mixture was cooled down to room temperature and filtered through celite. The filtrate was concentrated under reduced pressure. The oily residue was precipitated by methanol and the crude product **3** was filtered which is ready to be used in the next step. To the mixture of compound **3** (2.87 g, 8 mmol) and ethyl 4-hydroxybenzoate (1.33 g, 8 mmol) in cyclohexanone (30 mL) was added K_2CO_3 (672 mg, 12 mmol) and KI (133 mg, 0.8 mmol). After stirring at 140 °C for 3 h, the reaction mixture was cooled down to room temperature and filtered through celite. The filtrate was concentrated and the residue was purified by column chromatography over silica gel with hexane/EtOAc to give the compound **4** (2.84 g, 80%) as a white solid. ^{1}H NMR (400 Hz, $CDCl_3$): δ 8.00-7.97 (m, 2H, ArH), 7.70–7.63 (m, 4H, ArH), 7.54-7.51 (m, 2H, ArH), 7.00-6.98 (m, 2H, ArH), 6.91-6.89 (m, 2H, ArH), 4.37-4.32 (q, 2H, J = 6.8 Hz, OCH_2), 4.05-4.02 (m, 4H, OCH_2O), 1.87-1.84 (m, 4H, CH_2), 1.59-1.55 (m, 4H, CH_2), 1.40-1.36 (t, 3H, J = 7.2 Hz, CH_3); ^{13}C NMR (100 Hz, $CDCl_3$): δ 166.4, 162.8, 159.7, 145.2, 132.6(×4), 131.5, 131.3, 128.3 (×2), 127.0 (×2), 119.1, 115.1 (×2), 114.0 (×2), 110.0, 67.9 (×2), 60.6, 29.1, 29.0, 25.9, 25.8, 14.4.

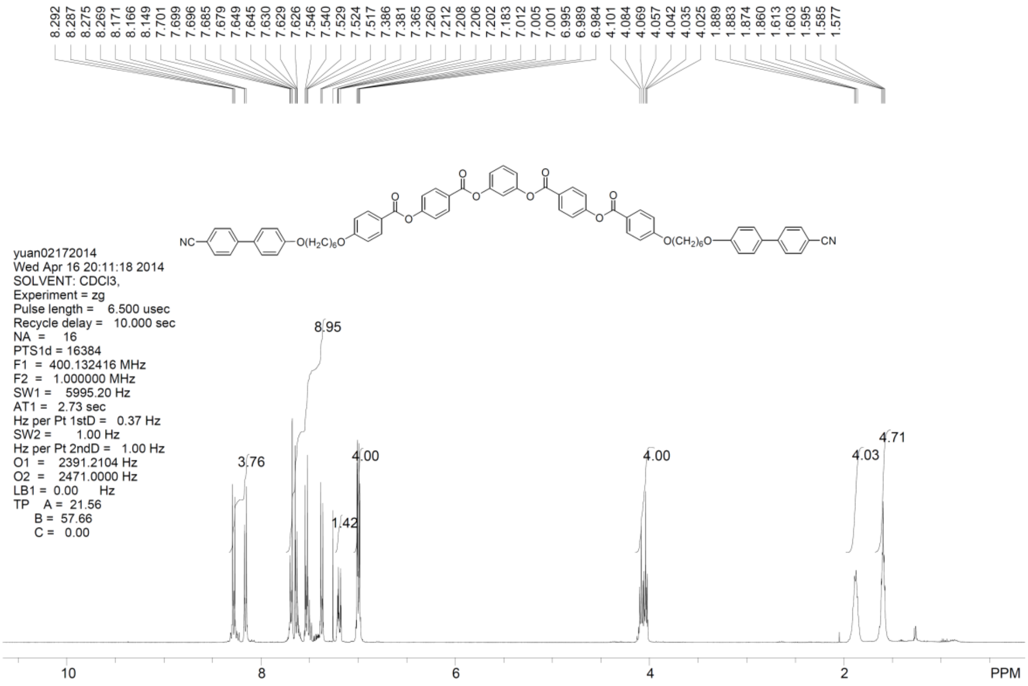
2.2. 4-Formylphenyl 4-((6-((4'-isocyano-[1,1'-biphenyl]-4-yl)oxy)hexyl)oxy) benzoate (6)

To the solution of compound **4** (2.84 g, 6.4 mmol) in ethanol/tetrahhedrofuran (30 mL/30 mL) was added aqueous KOH (0.24 mL, 5 M) and the solution was refluxed for 3 h. After cooling to the room temperature, the mixture was acidified by HCl. The precipitite was filtered and rasined by water and ethanol. The obtained white solid **5** was dried in vaccum oven and ready to be used in the next step. The compound **5** (1 g, 2.4 mmol) in thionyl chloride (50 mL) was refluxing for 4 h. After the thionyl chloride was removed, the residue was dissolved in THF (45 mL). Then triethylamine (2.44 g, 24 mmol) and 4-hydroxybenzaldehyde (880 mg, 7.2 mmol) in THF (15 mL) was added dropwisely in the solution. This solution was refluxing for 12 h and then cooled to room temperature. The solvent was removed by vaccum evaporation and the residue was purified by column chromatography over silica gel with hexane/EtOAc/dichloromethane to give the compound **6** (1.06 g, 85%) as a white solid. ^{1}H NMR (400 Hz, $CDCl_3$): δ 10.02 (s, 1H, CHO), 8.15-8.13 (m, 2H, ArH), 7.98-7.96 (m, 2H, ArH), 7.70-7.62 (m, 4H, ArH), 7.54-7.39 (m, 4H, ArH), 7.00-6.98 (m, 4H, ArH), 4.13-4.02 (m, 4H, OCH_2O), 1.93-1.87 (m, 4H, CH_2), 1.63-1.57 (m, 4H, CH_2); ^{13}C NMR (100 Hz, $CDCl_3$): δ 191.0, 163.8 (×2), 159.7, 155.9, 145.2, 133.9, 132.7, 132.6(×2), 132.4 (×2), 131.2(×2), 128.3 (×2), 127.1 (×2), 122.6 (×2), 119.1, 115.0 (×2), 114.4 (×2), 68.2, 67.9, 29.1, 29.0, 25.8, 25.8.

2.3. Liquid crystal trimer 1

Solid $KMnO_4$ (967 mg, 6.12 mmol) was added to a solution of the compound **6** (1.06 g, 2.04 mmol) in acetone (50 mL) and the mixture was stirred at room temperature for 12 h. Aqueous $NaHSO_3$ (1.52 g, 6.12 mmol) was added and the mixture was stirred for 1 h and poured into aqueous 2 N HCl. The resulting white precipitate **7** was filtered and washed with water and dried under vaccum. To a suspension of the acid **7** (1.00 g, 1.87 mmol) in tetrahydrofuran/dichloromethane (30 mL/30 mL) was added resorcinol (68 mg, 0.62 mmol) and 4-dimethylaminopyridine (454 mg, 3.72 mmol). After stirring for 30 min, 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (713 mg, 3.72 mmol) was added. The mixture was stirred for 12 h at room temperature and diluted by D.I. water then. The mixture was extracted by dichloromethane (30 mL × 3) and the organic phase was washed with D.I. water (30 mL × 2) and brine (30 mL). After dried over Na_2SO_4, the solvent was evaporated and the residue was purified by column chromatography over silica gel with hexane/EtOAc/dichloromethane. The further purification was achieved by recrystallization in dichloromethane/ethanol, giving the target bent-core liquid crystal trimer **1** (461 mg, 65%) as a white solid. ^{1}H NMR (400 Hz, $CDCl_3$): δ 8.29-8.15 (m, 4H, ArH), 7.70-7.37 (m, 9H, ArH), 7.21-7.18 (m, 1H, ArH), 7.01-6.98 (m, 4H, ArH), 4.10-4.02 (m, 4H, OCH_2), 1.89-1.86 (m, 4H, CH_2), 1.61-1.57 (m, 4H, CH_2); ^{13}C NMR (100 Hz, $CDCl_3$): δ 164.3, 164.1, 163.7, 159.7, 155.4, 151.4, 145.2, 132.6(×2), 132.5(×2), 132.4(×2), 131.8, 128.3 (×2), 127.0(×2), 126.6(×2), 122.1(×2), 121.0, 119.3, 119.1(×2), 115.0(×2), 114.4(×2), 68.1, 67.9, 29.1, 29.0, 25.8, 25.8. Elemental analysis cald for $C_{72}H_{60}N_2O_{12}$: C 75.51, H 5.28, N 2.45, found C 75.28, H 5.24, N 2.34.

2.3.1 ^{1}H and ^{13}C NMR spectra of timer 1



yuan02172014
Wed Apr 16 20:11:18 2014
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Recycle delay = 10.000 sec
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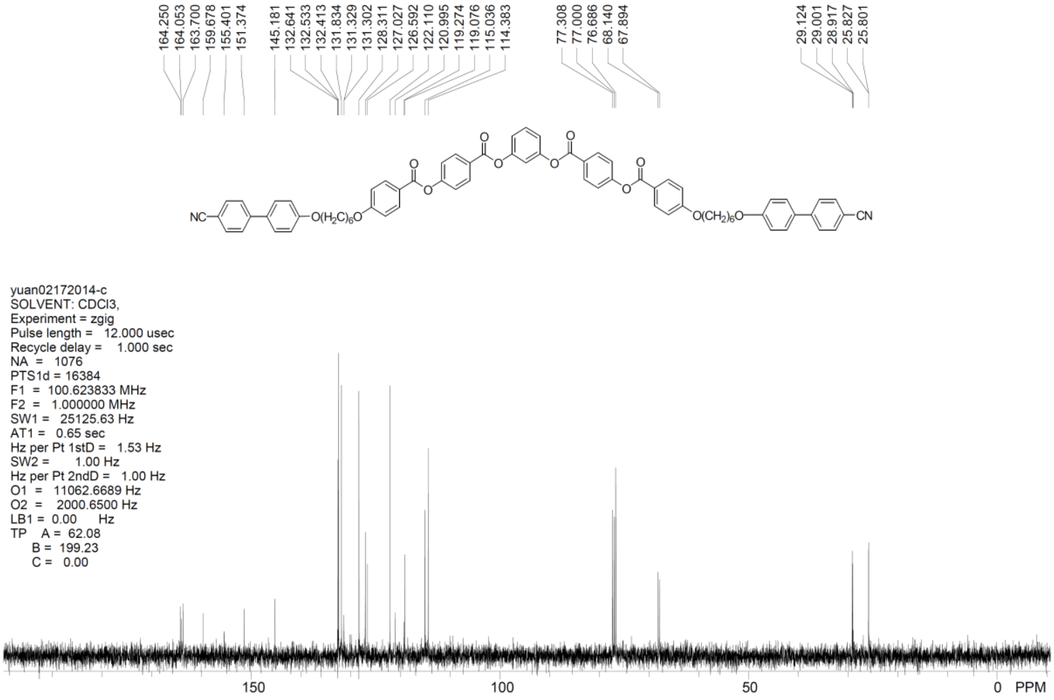
F1 = 400.132416 MHz
F2 = 1.000000 MHz
SW1 = 5995.20 Hz
AT1 = 2.73 sec
Hz per Pt 1stD = 0.37 Hz
SW2 = 1.00 Hz
Hz per Pt 2ndD = 1.00 Hz
O1 = 2391.2104 Hz
O2 = 2471.0000 Hz
LB1 = 0.00 Hz
TP A = 21.56
B = 57.66
C = 0.00

Fig. S1 ^{1}H NMR spectra of timer **1**



yuan02172014-c
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F2 = 1.000000 MHz
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AT1 = 0.65 sec
Hz per Pt 1stD = 1.53 Hz
SW2 = 1.00 Hz
Hz per Pt 2ndD = 1.00 Hz
O1 = 11062.6689 Hz
O2 = 2000.6500 Hz
LB1 = 0.00 Hz
TP A = 62.08
B = 199.23
C = 0.00

Fig. S2 ^{13}C NMR spectra of timer **1**

2.3.2 The result of differential scanning calorimetry (DSC) for the bent-core liquid crystal trimer 1

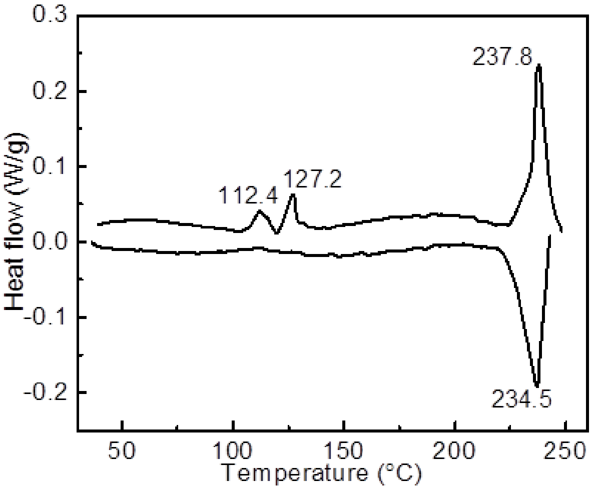

Fig. S3 DSC thermograph of trimer **1** during the first heating and cooling cycle with rate 5 °C/min

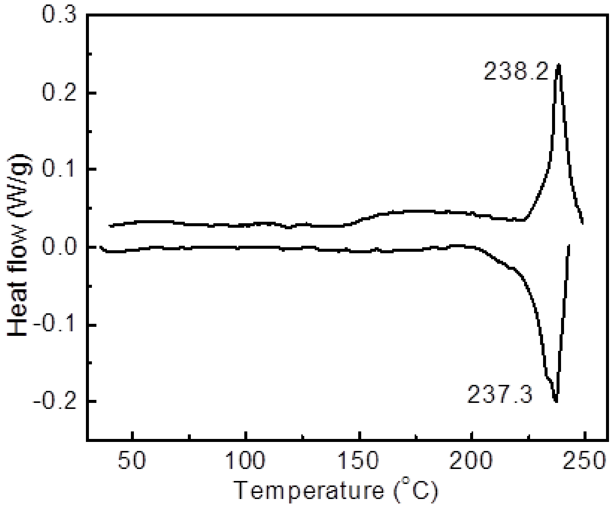

Fig. S4 DSC thermograph of trimer **1** during the second heating and cooling cycle with rate 5 °C/min

2.3.3 Temperature-dependence of 2D XRD patterns

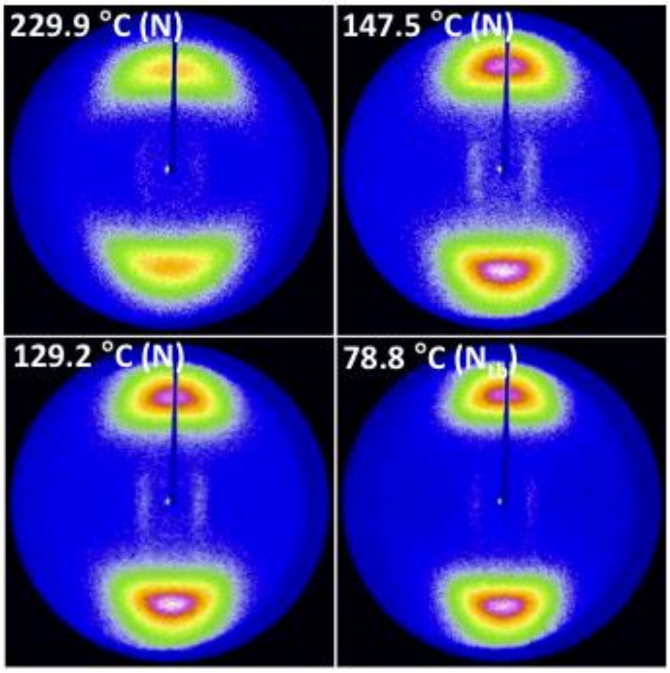

Fig. S5 The 2D XRD patterns at different temperatures in N and N$_{tb}$ phases of *trimer* **1** a magnetically aligned sample. The temperature and the phase in which the patterns were obtained are indicated in the figure.